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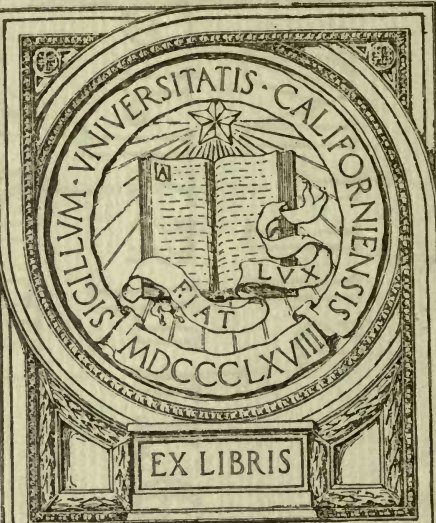


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EXCHANGE



EX LIBRIS



The Electrical Conductivity  
of  
Certain Salts In Pyridine

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THESIS

SUBMITTED TO THE FACULTY OF THE GRADUATE COLLEGE  
OF THE STATE UNIVERSITY OF IOWA IN PARTIAL  
FULFILLMENT OF THE REQUIREMENTS  
FOR THE DEGREE OF DOCTOR  
OF PHILOSOPHY

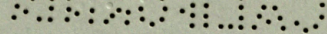
BY  
EDWARD X. ANDERSON  
IOWA CITY, IOWA



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EASTON, PA.:  
ESCHENBACH PRINTING CO.  
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EXCHANGE



# THE ELECTRICAL CONDUCTIVITY OF CERTAIN SALTS IN PYRIDINE

BY EDWARD X. ANDERSON

## Introduction

Thus far little work of a systematic nature has been done on the electrical conductivity of salts in pyridine, and this has been limited in every case to one temperature and to the more dilute solutions. Laszczynski and Gorski<sup>1</sup> investigated the conductivity of pyridine solutions containing lithium chloride, and the iodides and thiocyanates of potassium, sodium and ammonium, all measurements being made at 18°. They found that the equivalent curves showed sufficient convergence to render possible the calculation of  $l_{\infty}$  by extrapolation, where  $l_{\infty}$  represents the equivalent electrical conductivity of the solutions at infinite dilution. The maximum values of the equivalent conductivity lie between 40 and 46, and they are, therefore, as large as the values obtained, using ethyl alcohol as a solvent. Lithium chloride showed scarcely any dissociation. Lincoln<sup>2</sup> found that various inorganic salts yielded conducting solutions in pyridine, but values for  $l_{\infty}$  are rarely encountered. Dutoit and Duperthus<sup>3</sup> determined the conductivities of pyridine solutions containing potassium iodide, potassium thiocyanate and sodium thiocyanate, for dilutions ranging from 1,000 to 20,000 liters per gram-mole of salt. Within these limits Ostwald's dilution law applies in most cases, thus rendering it possible to calculate the degree of dissociation at any given dilution.

Jones and West<sup>4</sup> studied the temperature coefficients of conductivity in aqueous solutions and the effect of temperature on dissociation. In their work the following rela-

<sup>1</sup> Zeit. Elektrochemie, **4**, 290-293 (1897).

<sup>2</sup> Jour. Phys. Chem., **3**, 457-484 (1899).

<sup>3</sup> Jour. chim. phys., **6**, 699-725 (1909).

<sup>4</sup> Am. Chem. Jour., **34**, 357 (1905); **35**, 445 (1906).



tions were found to exist: a rise in temperature, ranging from  $0^{\circ}$  to  $35^{\circ}$  produces a large increase in conductivity due to an increase in ionic mobility. This last effect results from a reduction in viscosity and a simplification of complexes. For any given electrolyte the temperature coefficients of conductivity increase with increasing dilution; with different electrolytes this increase is greatest for those electrolytes with large hydrating power. Voellmer<sup>1</sup> found that the temperature coefficients of electrical conductivity increased with rising dilution for solutions of lithium chloride, and the acetates and iodides of potassium and sodium in methyl alcohol, and also for the solutions of sodium chloride, calcium chloride, silver nitrate and calcium nitrate in ethyl alcohol. The molecular conductivities of various concentrations of the chlorides of nickel, manganese and cobalt in methyl alcohol, ethyl alcohol and acetone, between  $0^{\circ}$  and  $45^{\circ}$ , were studied by Rimbach and Weitzel.<sup>2</sup> In contrast with the near constancy of the temperature coefficients on dilution in aqueous solutions, they found that in organic solvents the temperature coefficients increase, as a rule, with increasing dilution. An examination of the work of Jones and Clover,<sup>3</sup> and of Jones and West,<sup>4</sup> however, shows that the temperature coefficients of conductivity in aqueous solutions do increase with increase in dilution and in most cases the increase is quite pronounced.

The results obtained and the conclusions made by the above investigators will be considered more fully in the discussion of the present work.

Pyridine, like water, has the power of combining with salts to form crystalline solids with pyridine of crystallization. This being the case, according to the law of mass action, one should expect these salts to combine with a much larger amount of pyridine when in solution in this solvent.

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<sup>1</sup> Wied. Ann., **52**, 328 (1894).

<sup>2</sup> Zeit. phys. Chem., **79**, 279 (1912).

<sup>3</sup> Am. Chem. Jour., **43**, 187 (1910).

<sup>4</sup> Loc. cit.



Further, as in the case of hydrates, one should expect the complexity of these ionic "pyridinates" to be greatest in the most dilute solutions, and also that the complexity of the solvate at any given dilution should decrease with rise in temperature. This is based on the general law that, the stability of complexes decreases with the rise in temperature. Since pyridine tends to form these "pyridinates," interesting results might well be expected which, in a certain sense, are parallel to those obtained in aqueous solutions.

It was, therefore, thought worth while to make a careful, systematic study of the conductivity of solutions of various salts in pyridine at different temperatures and over as wide a range of concentrations as the experimental conditions would permit.

### Experimental

For measuring the conductivity the well known Kohlrausch method, consisting of the Wheatstone bridge, induction coil and telephone receiver, was used. The resistance boxes were certified by the Reichsanstalt and the Bureau of Standards.

The conductivity cells, three in number, were of the type first used by Jones and Lindsay.<sup>1</sup> These were provided with ground glass stoppers and sealed-in electrodes. A 0.02 *N* potassium chloride solution was used, in determining the cell constants. The "chemically pure" potassium chloride was recrystallized from conductivity water and carefully dried by heating for some time at a dull red heat and then cooled in a desiccator. The salt was then dissolved in conductivity water prepared by the method of Jones and Mackay.<sup>2</sup> This water had a specific conductance of  $1.5 \cdot 10^{-6}$  r. o. at 25°. The specific conductances of the 0.02 *N* potassium chloride at 0° and 25° were taken as 0.001522 and 0.002768, respectively.<sup>3</sup> The cell constants thus determined were then checked against 0.002 *N* potassium chloride. One set of

<sup>1</sup> *Zeit. phys. Chem.*, **56**, 129 (1906).

<sup>2</sup> *Am. Chem. Jour.*, **19**, 90 (1897).

<sup>3</sup> Ostwald-Luther: *Messungen*, third ed., 474.

constants used for the three cells were 0.0438, 0.2176 and 0.3985, respectively, and the values of  $l_0$  for 0.002 *N* potassium chloride checked to within 0.3 percent.

"Chemically pure" pyridine was allowed to stand over fused caustic potash for several months. It was then decanted and distilled. The fraction passing over between 115° and 116.1° at 74.5 cms was collected, the first and last portions being rejected. The specific conductance at 0° was found to be  $0.057 \cdot 10^{-7}$  r. o., at 25°,  $0.74 \cdot 10^{-7}$  and at 50°,  $1.2 \cdot 10^{-7}$ . Lincoln<sup>1</sup> found the specific conductance of this pyridine to be  $7.6 \cdot 10^{-7}$  at 25°, a much larger value.

Unless otherwise indicated, it will be understood that Kahlbaum's best grade "C. P." chemicals were used. After complete dehydration, by methods to be mentioned later, the salts were preserved in tightly stoppered weighing bottles over phosphorus pentoxide. Trial solubility tests were made to determine approximately the amount of each salt required for saturation at room temperature. Those salts which do not show hygroscopic properties were weighed out directly and the exact amounts required for a normality conveniently close to that of complete saturation was taken, but for those salts which tend to absorb moisture the method of weighing by difference was used. In diluting the mother solutions every possible care was taken to prevent contact with moisture. Suction was applied directly to the pipette through a calcium chloride drying tube.

All the solutions were prepared at room temperatures, 21°–22°, and transferred to tightly fitting glass-stoppered bottles. The conductivity measurements were made as soon after preparation as possible.

The capacities of the 25° and 50° baths used were 20 and 16 liters, respectively. They were heated by means of immersed electric lights, which were automatically operated by means of a contact toluol regulator and relay system. Stirrers, propelled by a small motor, were used to agitate the

<sup>1</sup> Jour. Phys. Chem., 3, 457 (1899).



water vigorously and thereby maintain a uniform temperature throughout the baths. By this means both temperatures were automatically kept at  $25^{\circ} \pm 0.02$  and  $50^{\circ} \pm 0.05$ . A mixture of well washed, finely crushed ice moistened with distilled water was used for the  $0^{\circ}$  bath. The order of temperatures followed for the conductivity measurements was  $25^{\circ}$ ,  $0^{\circ}$  and  $50^{\circ}$ . The temperature  $25^{\circ}$  was selected as the initial, because the solutions were made up at room temperature. Thermal equilibrium would, therefore, be more quickly attained at this temperature than at either of the others. The temperature  $0^{\circ}$  was selected as the second in order to permit of the minimum change in the concentration of the solutions by condensation of pyridine on the inside wall of the cells. If the cells had been immersed in the  $50^{\circ}$  bath before being subjected to a temperature of  $0^{\circ}$ , there would be more pyridine condensed on the cell walls than if the  $25^{\circ}$  immediately preceded the  $0^{\circ}$  bath. Forty minutes were found to be sufficient for establishing thermal equilibrium, because by trial experiments the conductivity was found to remain constant after this amount of time had elapsed.

*Silver Nitrate.*—The pure crystals were pulverized and kept in the dark over phosphorus pentoxide for several days. This salt dissolves in pyridine with a considerable evolution of heat, probably due to the formation of  $\text{AgNO}_3 \cdot 2\text{Pyr}$ , or  $\text{AgNO}_3 \cdot 3\text{Pyr}$ , both of which have been found capable of existing in the solid phase.<sup>1</sup> Kahlenberg and Brewer<sup>2</sup> found  $\text{AgNO}_3 \cdot 3\text{Pyr}$  to be stable between  $-24^{\circ}$  and  $+48.5^{\circ}$ , where it changes to  $\text{AgNO}_3 \cdot 2\text{Pyr}$ . Below  $-24^{\circ}$  the compound  $\text{AgNO}_3 \cdot 6\text{Pyr}$  is the stable form.

In the following data V denotes the volume of the solution in liters containing one gram-equivalent weight of the salt.  $l_0$ ,  $l_{25}$  and  $l_{50}$  represent the equivalent conductivities of the various solutions at  $0^{\circ}$ ,  $25^{\circ}$  and  $50^{\circ}$ , respectively. The temperature coefficients are headed by the letters A, B and C where

<sup>1</sup> Reitzenstein: Liebig's Ann., 282, 267 (1894).

<sup>2</sup> Jour. Phys. Chem., 12, 283 (1908).



$$A = \frac{l_{25} - l_0}{l_0 \cdot 25}, B = \frac{l_{50} - l_{25}}{l_{25} \cdot 25} \text{ and } C = \frac{l_{50} - l_0}{l_0 \cdot 50}.$$

In the curves which follow, the cube roots of the volumes in cubic centimeters are plotted as abscissae, against the equivalent conductivity  $l$  as ordinates. Each space along the abscissa is equal to 2.5 units after the root is extracted. Every space along the ordinate is equal to 10 units after the equivalent conductivity is multiplied by the factor, which will be specified in each case. This factor is used in order to magnify the trend of the curves. It must also be remembered that any errors are likewise highly magnified.

TABLE I

V	$l_0$	$l_{25}$	$l_{50}$
1	1.05	1.55	2.01
2	14.77	19.38	23.28
10	20.68	25.38	27.25
20	22.38	27.05	29.17
100	27.80	34.49	37.92
500	37.31	47.63	55.10

TABLE II

V	A	B	C
1	0.0149	0.0121	0.0183
2	0.0125	0.0081	0.0115
10	0.0091	0.0029	0.0064
20	0.0084	0.0031	0.0061
100	0.0096	0.0040	0.0073
500	0.0111	0.0063	0.0095

From Fig. I it will be seen that, with dilution the equivalent conductivity of silver nitrate increases at first very rapidly and then less rapidly with further dilution for all three temperatures. They do not appear to approach maximum values. The values for  $l_v$  here given agree very closely with those given by Lincoln<sup>1</sup> for the same salt at 25°. The tempera-

<sup>1</sup> Loc. cit.



ture coefficients (Table II) show distinct minima, decreasing at first very rapidly and then increasing very slowly on further dilution. Although solutions of silver nitrate in pyridine possess a relatively high molecular conductivity, Walden and Centnerszwer<sup>1</sup> found that the molecular weights of silver nitrate in dilute pyridine solutions are normal, while

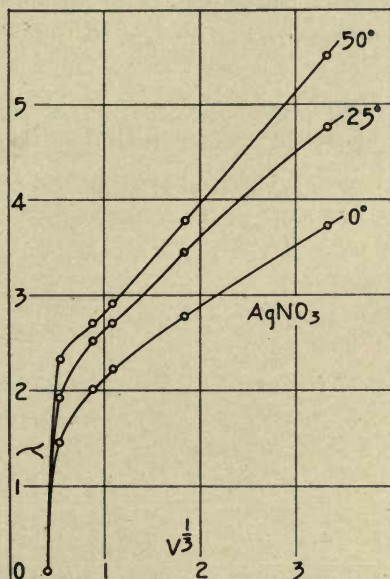
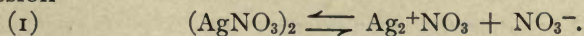


Fig. I

in concentrated solutions (0.1 *N* to 1.0 *N*) the molecular weights are greater than normal, thus indicating association. By the same method Schmuilow<sup>2</sup> found that this salt is apparently non-ionized. Since transference measurements made by Neustadt and Abegg<sup>3</sup> showed that both  $\text{Ag}^+$  ions and  $\text{NO}_3$  radicle migrated toward the cathode, they assumed that, if ionization does take place, it does so according to the expression

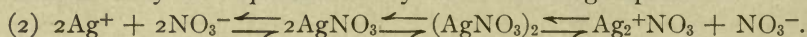


<sup>1</sup> Zeit. phys. Chem., **55**, 321 (1906).

<sup>2</sup> Zeit. anorg. Chem., **15**, 18 (1897).

<sup>3</sup> Zeit. phys. Chem., **69**, 486 (1910).

That simple  $\text{Ag}^+$  ions are also present to a slight extent is not to be doubted, and, therefore, the more complete equilibrium may be represented by the following equation:



*Lithium Chloride.*—The sample was heated at  $120^\circ$  for several days, with frequent pulverizing in a hot agate mortar until the tendency to cake ceased. The dry, finely powdered salt was preserved in a tightly stoppered weighing bottle.

Lithium chloride dissolves in pyridine with a evolution of heat; it separates from solution as  $\text{LiCl} \cdot 2\text{Pyr}$ .<sup>1</sup>

TABLE III

V	$l_0$	$l_{25}$	$l_{60}$
0.59	0.143	0.199	0.239
1.00	0.218	0.264	0.282
2.00	0.254	0.290	0.299
10.00	0.279	0.322	0.346
100.00	0.519	0.573	0.613
1000.00	1.47	1.60	1.68

TABLE IV

V	A	B	C
0.59	0.0160	0.0079	0.0135
1.00	0.0083	0.0028	0.0058
2.00	0.0056	0.0012	0.0035
10.00	0.0061	0.0030	0.0047
100.00	0.0041	0.0028	0.0036
1000.00	0.0037	0.0020	0.0029

An examination of Table III and Fig. II shows that lithium chloride is at best a very poor conductor and is but slightly dissociated at all concentrations and temperatures. The equivalent conductivities do, however, show a rapid increase at first, and then very slight and finally more rapidly, with increasing dilution. The values found by Laszczynski and Gorski<sup>2</sup> for the same solutions are about four times as

<sup>1</sup> Laszczynski: Ber. deutsch. chem. Ges., 27, 2285 (1894).

<sup>2</sup> Loc. cit.



large, due, perhaps, to the presence of a slight trace of moisture. Increasing dilution has a marked initial effect on the

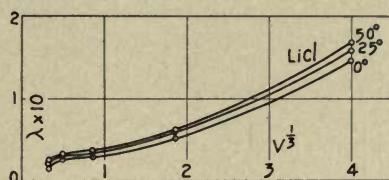


Fig. II

temperature coefficients (Table IV), the latter passing through a minimum.

*Lithium Bromide.*—The anhydrous salt was prepared in a manner similar to that used for lithium chloride.

TABLE V

V	$l_0$	$l_{25}$	$l_{50}$
0.98	—	1.29	1.65
2.00	0.98 <sup>1</sup>	1.72	1.98
10.00	2.29	2.44	2.40
100.00	5.43	5.34	4.89
1000.00	13.68	14.15	13.58
10,000.00	24.8	28.7	29.9
∞	(28.5)	(36.3)	(49.0)

TABLE VI

V	A	B	C
0.98	—	0.0109	—
2.00	0.0298 <sup>1</sup>	0.0061	0.0202
10.00	0.0026	—0.0006	0.0009
100.00	—0.0007	—0.0034	—0.0020
1000.00	0.0013	—0.0016	—0.0001
10,000.00	0.0063	0.0017	0.0041

A glance at Fig. III reveals the fact that the equivalent conductivity of lithium bromide increases steadily with increasing dilutions, but not at every dilution with a rise in temperature, there being in some cases a decrease in conduc-

<sup>1</sup> Solidified.

tivity with a rise in temperature. The values for  $l_{\infty}$  at  $0^{\circ}$ ,  $25^{\circ}$  and  $50^{\circ}$  were extrapolated and found to be 28.5, 36.3 and 49.0, respectively. The near proximity of the curves signifies that a change in temperature has little effect on the conductivity, there being a slight increase in this effect in

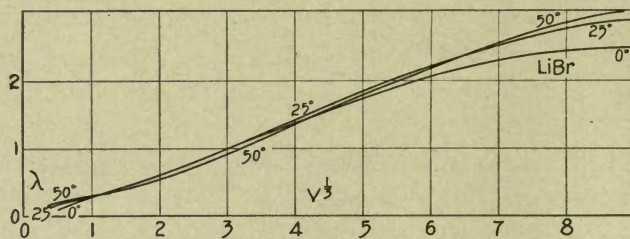


Fig. III

the more dilute solutions. The values for the temperature coefficients (Table VI) decrease, at first, with increasing dilution. This decrease is quite rapid in the more concentrated solutions, passing through minima of negative values and then finally increasing at an almost constant rate.

*Lithium Iodide.*—The salt was carefully dehydrated by constant heating for several days and nights.

TABLE VII

V	$l_0$	$l_{25}$	$l_{50}$
1.0	4.40	7.04	9.82
2.0	7.79	10.98	13.82
10.0	12.76	16.40	18.62
100.0	18.34	23.35	25.98
1000.0	27.10	35.99	42.65
10,000.0	31.2	44.4	50.5
$\infty$	(31.2)	(44.9)	(50.5)

TABLE VIII

V	A	B	C
1.0	0.0224	0.0158	0.0246
2.0	0.0164	0.0103	0.0155
10.0	0.0114	0.0054	0.0092
100.0	0.0109	0.0045	0.0083
1000.0	0.0131	0.0074?	0.0115
10,000.0	0.0169	0.0055	0.0124
$\infty$	(0.0180)	(0.0050)	(0.0124)



From Fig. IV it is observed that lithium iodide is a good conductor. The conductivity increases quite rapidly at the outset, but continuously increases at a decreasing rate and soon attains maximum values. The  $0^\circ$  and  $50^\circ$  curves appear to be asymptotic at a dilution of ten thousand liters; the values for  $l_v$  which were actually obtained at this dilution are, therefore, taken as those for  $l_\infty$  and are 31.2 and

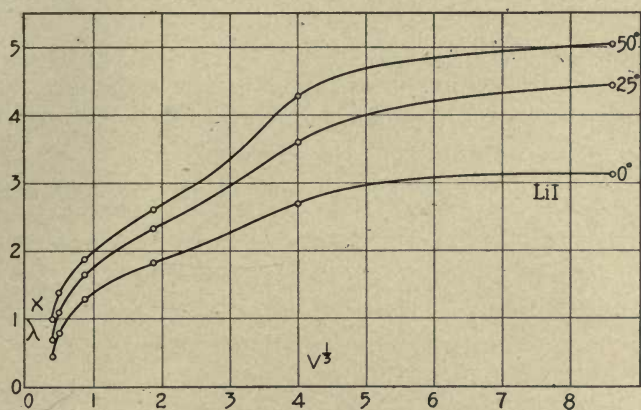


Fig. IV

50.5, respectively. By extrapolation the value for  $l_\infty$  at  $25^\circ$  is found to be 44.9. The temperature coefficients fall exceedingly rapidly to minima and then increase very slowly with increasing dilution.

*Sodium Iodide.*—The finely powdered salt was thoroughly dried at a temperature slightly exceeding  $100^\circ$ . This substance dissolves in pyridine with considerable evolution of heat.

TABLE IX

V	$l_0$	$l_{25}$	$l_{50}$
1.33	0.11 <sup>1</sup>	0.70	0.84
5.00	10.00	11.14	11.20
10.00	14.56	16.15	15.80
100.00	21.66	23.81	22.87
1000.00	32.99	39.53	41.28
10,000.00	42.20	56.70	63.20

<sup>1</sup> Solid present.

TABLE X

V	A	B	C
1.33	0.2084 <sup>1</sup>	0.0076	0.1279 <sup>1</sup>
5.00	0.0046	0.0002	0.0024
10.00	0.0044	—0.0009	0.0017
100.00	0.0040	—0.0016	0.0011
1000.00	0.0079	0.0018	0.0050
10,000.00	0.0137	0.0046	0.0099

An examination of Table IX and Fig. V reveals the fact that  $l_v$  follows the same general trend as the preceding curves; again, the values of  $l_v$  increase on dilution most rapidly in the concentrated solutions. By extrapolation  $l_\infty$  was found to be 43.3 at 0°. Laszczynski and Gorski<sup>2</sup> obtained 44.32

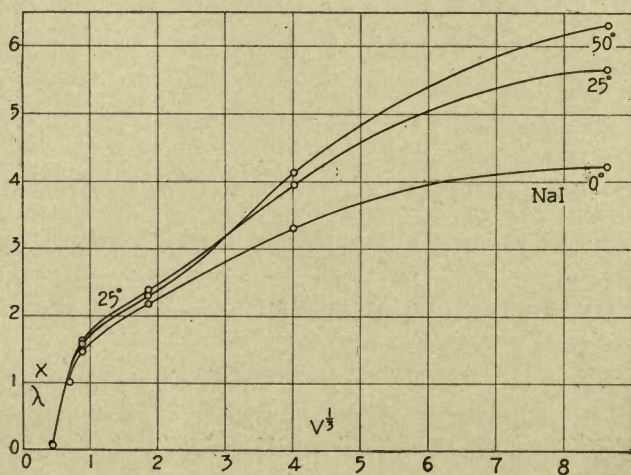


Fig. V

for the value of  $l_\infty$  at 18°. For 25° and 50°, however, maximum values could not be obtained by extrapolation. At these temperatures the equivalent conductivities continue to increase with dilution more rapidly than at 0°.

The temperature coefficients show well marked minima.

<sup>1</sup> Solid phase present.

<sup>2</sup> Loc. cit.



Here, again, negative values appear for temperatures between 25° and 50°.

*Potassium Thiocyanate.*—The sample used was crystallized from absolute alcohol, washed with absolute alcohol, and dried at 95°. This salt differs from the others studied in that its solubility in pyridine decreases as the temperature rises.

TABLE XI

V	$l_0$	$l_{25}$	$l_{50}$
7.0	5.97	7.12	7.75
14.0	7.20	8.45	9.00
70.0	11.40	13.36	14.54
140.0	14.17	16.77	18.14
1400.0	27.32	33.70	38.31
14,000.0	42.86	58.51	71.30

TABLE XII

V	A	B	C
7.0	0.0077	0.0035	0.0060
14.0	0.0069	0.0026	0.0050
70.0	0.0070	0.0035	0.0055
140.0	0.0073	0.0033	0.0056
1400.0	0.0093	0.0055	0.0081
14,000.0	0.0146	0.0087	0.0133

Referring to Fig. VI, it is obvious that the equivalent conductivity of potassium thiocyanate increases at a more constant rate than most of the conductivities of the preceding salts. By extrapolation 46.5 is obtained for the value of  $l_\infty$  at 0°. Laszczynski and Gorski<sup>1</sup> give values in fair agreement with the above, tabulated, comparisons being made at 18°. They did not obtain a value for  $l_\infty$  inasmuch as the dilutions at which they worked did not exceed 2870.4 liters. However, the data which they give show that the conductivity is approaching a maximum value. The temperature coefficients exhibit slight minima. In aqueous solutions

<sup>1</sup> Loc. cit.

the effect of dilution upon the temperature coefficients is greatest in the most dilute solutions, as we should expect.

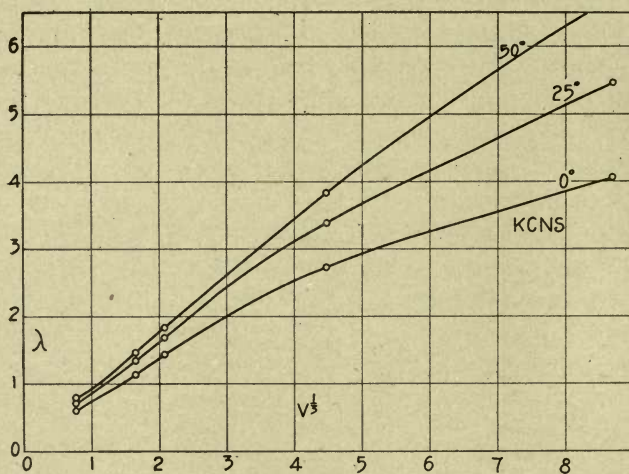


Fig. VI

*Ammonium Thiocyanate*.—The anhydrous salt was prepared in the same manner as the potassium thiocyanate.

TABLE XIII

V	$l_0$	$l_{25}$	$l_{50}$
0.33	2.10	4.46	7.43
1.00	8.21	11.70	15.12
2.00	10.45	13.76	16.53
10.00	11.96	14.56	16.29
100.00	17.00	20.33	22.18
1000.00	33.57	41.80	47.76

TABLE XIV

V	A	B	C
0.33	0.0451	0.0266	0.0508
1.00	0.0170	0.0117	0.0169
2.00	0.0127	0.0081	0.0116
10.00	0.0087	0.0048	0.0072
100.00	0.0078	0.0036	0.0061
1000.00	0.0098	0.0057	0.0085



From Fig. VII it will be observed that the equivalent conductivity of ammonium thiocyanate behaves somewhat peculiarly, when compared with the previous curves. The conductivity curves rise rapidly at first and then approximate parallelism with the volume axis in the more concentrated solutions, and then increase again with increasing dilution. The values for  $l_v$  given in the above table are somewhat larger than those given by Laszczynski and Gorski. They carried the dilution out to 2080 liters and were able to calculate the values for  $l_\infty$ , which they give as 40.22. In the above curves it may be clearly seen that the 0° curve gives

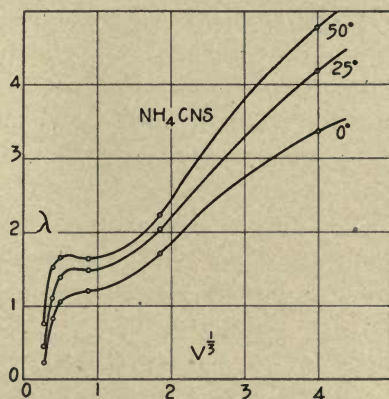


Fig. VII

promise of a maximum value for  $l_v$ , but the 25° and 50° curves show practically no signs of such a tendency. In connection with the strange conduct of the curves in the vicinity of concentrated solutions, it may be pointed out that the temperature coefficients show equally striking changes, dropping suddenly to minima, and then increasing very slowly in the dilute solutions.

A relation, exactly analogous to that of the conductivity values shown above, was observed by Franklin<sup>1</sup> for ammonium thiocyanate and tetramethylammonium iodide in liquid sulphur dioxide. The conductivity curves of tetra-

<sup>1</sup> Jour. Phys. Chem., 15, 675-97 (1911).

methyllumonium iodide in liquid sulphur dioxide are almost identical in form with those here represented for ammonium thiocyanate in pyridine, while those for ammonium thiocyanate in the same solvent are not very unlike those obtained in pyridine. Upon passing from the most concentrated solutions to the most dilute, Franklin found that the molecular conductivity first increases to a maximum, then falls to a minimum value, and finally approaches the usual maximum on further dilution. He explained these results by assuming that the dissociated salt is auto-ionized in the concentrated solutions and that this effect decreases with dilutions. On the other hand, the decrease in viscosity with dilution causes a rise in ionic mobility. These two effects balance each other at the first mentioned maximum. On further dilution the auto-ionization disappears and the conductivity from then on is due to the dissociating power of the solvent. Concentrated solutions of ammonium thiocyanate in pyridine are very viscous; the same is true of a concentrated solution of ammonium thiocyanate in liquid sulphur dioxide.<sup>1</sup> The initial rapid increase in the equivalent conductivities and decrease in temperature coefficients are undoubtedly chiefly due to a rapid decrease in viscosity with slight change in dilution. It is a singular fact that Franklin<sup>2</sup> found the minimum temperature coefficient of conductivity to exist in the solutions of intermediate dilution, where the minimum conductivity was also found. This is in accord with the results here given for ammonium thiocyanate in pyridine. On the other hand, for sulphur dioxide the minimum value of the equivalent conductivity is displaced toward the region of greater dilution, with rising temperature, but this is not so for solutions of the same salt in pyridine. It seems, therefore, that the disturbing influences acting on ammonium thiocyanate when dissolved in liquid sulphur dioxide are, at least in some measure, at work in pyridine.

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<sup>1</sup> Franklin: *Loc. cit.*

<sup>2</sup> *Loc. cit.*



*Mercuric Chloride.*—The sample used was recrystallized from conductivity water and thoroughly dried at  $100^{\circ}$ – $105^{\circ}$ .

Lang<sup>1</sup> and Reitzenstein<sup>2</sup> have studied the compound  $\text{HgCl}_2 \cdot \text{Pyr}$ , and the formation of  $\text{HgCl}_2 \cdot 2\text{Pyr}$  has been investigated by Pesci.<sup>3</sup> McBride<sup>4</sup> determined the temperature-solubility curve for mercuric chloride in pyridine at temperatures ranging from  $-33^{\circ}$  to  $+145^{\circ}$  and proved the existence of the three compounds,  $\text{HgCl}_2 \cdot 2\text{Pyr}$ ,  $\text{HgCl}_2 \cdot \text{Pyr}$  and  $3\text{HgCl}_2 \cdot 2\text{Pyr}$ .

TABLE XV

V	$l_0$	$l_{25}$	$l_{50}$
0.5	0.009 <sup>1</sup>	0.036	0.045
1.0	0.019	0.025	0.030
2.0	0.016	0.021	0.025
10.0	0.016	0.021	0.027
100.0	0.037	0.061	0.067
1000.0	0.130	0.260	0.400

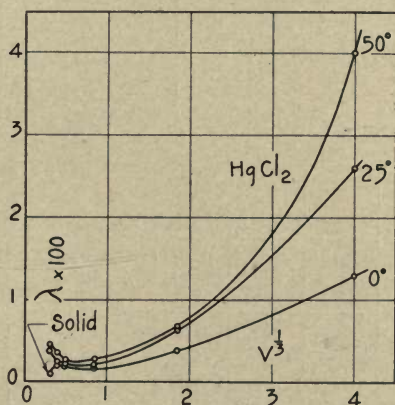


Fig. VIII

<sup>1</sup> Ber. deutsch. chem. Ges., **21**, 1578–88 (1888).

<sup>2</sup> Ann. Phys. Chem., **43**, 839–40 (1891).

<sup>3</sup> Gazz. chim. ital., **25**, II, 423–33 (1895).

<sup>4</sup> Jour. Phys. Chem., **14**, 189–200 (1910).

TABLE XVI

V	A	B	C
0.5	0.1176 <sup>1</sup>	0.0104	0.0793 <sup>1</sup>
1.0	0.0136	0.0076	0.0119
2.0	0.0126	0.0065	0.0105
10.0	0.0126	0.0119?	0.0141
100.0	0.0260	0.0039	0.0162
1000.0	0.0400	0.0215	0.0415

*Mercuric Bromide*.—This salt was precipitated from a solution of mercuric chloride with potassium bromide, recrystallized from and thoroughly washed with conductivity water and finally dried at 100°–105°.

Groos<sup>2</sup> and Reitzenstein<sup>3</sup> made the compound  $\text{HgBr}_2 \cdot 2\text{Pyr}$ .

TABLE XVII

V	$l_0$	$l_{25}$	$l_{50}$
0.5	0.012 <sup>1</sup>	0.034	0.043
1.0	0.020	0.026	0.032
2.0	0.018	0.023	0.026
10.0	0.017	0.023	0.028
100.0	0.031	0.047	0.053
1000.0	0.13	0.28	0.29

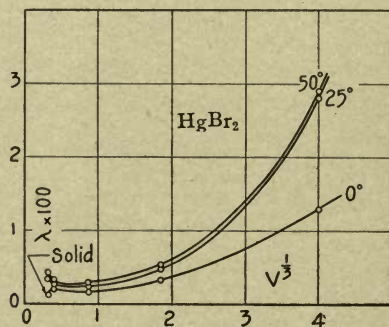


Fig. IX

<sup>1</sup> Solid phase present.

<sup>2</sup> Arch. Pharm., (3) 28, 73–8.

<sup>3</sup> Loc. cit.



TABLE XVIII

V	A	B	C
0.5	0.0742 <sup>1</sup>	0.0108	0.0525 <sup>1</sup>
1.0	0.0121	0.0090	0.0119
2.0	0.0104	0.0063	0.0092
10.0	0.0128	0.0092	0.0124
100.0	0.0207	0.0051	0.0142
1000.0	0.0462	0.0014	0.0246

*Mercuric Iodide.*—A method similar to that used for the preparation of mercuric bromide was followed in preparing this salt, using potassium iodide as the precipitant. Com-

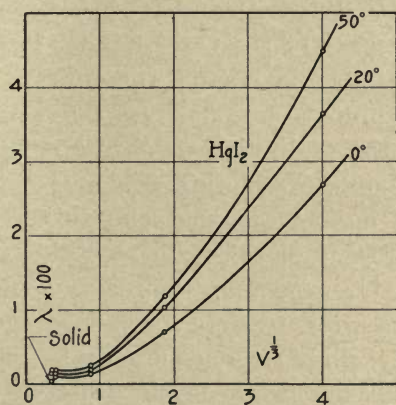


Fig. X

plete desiccation was assumed after the salt had been kept for some time at the transition point of the iodide.

The compound  $\text{HgI}_2 \cdot 2\text{Pyr}$  has been prepared by Groos.<sup>2</sup>

TABLE XIX

V	$l_0$	$l_{25}$	$l_{50}$
0.67	Solidified	0.013	0.018
1.00	0.009	0.013	0.018
2.00	0.008	0.012	0.015
10.00	0.013	0.019	0.024
100.00	0.069	0.102	0.117
1000.00	0.266	0.364	0.448

<sup>1</sup> Solid present.

<sup>2</sup> Loc. cit.

TABLE XX

V	A	B	C
0.67	—	0.0162	—
1.00	0.0186	0.0130	0.0188
2.00	0.0170	0.0118	0.0169
10.00	0.0198	0.0099	0.0173
100.00	0.0190	0.0059	0.0139
1000.00	0.0148	0.0093	0.0137

As a general rule the mercuric halides when dissolved in organic solvents exhibit a strong tendency either to polymerize, or to unite with the solvent to form complex solvent-solute molecules. Walden and Centnerszwer<sup>1</sup> determined the molecular weights of the three halides in pyridine by the boiling-point method and found them to be approximately normal in the dilute solutions. In the concentrated solutions, however, the molecular weights are less than normal, which, since the low conducting power is evidence of slight ionization, must indicate in the solution the presence of solvent-solute complex molecules and complex ions.

As was to be expected, the equivalent conductivities of the three salts are extremely low. The effect of temperature is relatively slight; the conductivity values for corresponding dilutions are of the same order of magnitude and show a minimum conductivity in the regions of greatest concentration.

The values of  $l_v$  for mercuric iodide are much smaller than those obtained by Lincoln<sup>1</sup> at 25°.

Owing to the low conductivity of these solutions and the fact that very slight errors are enormously magnified in the calculation, no emphasis is made of the exactness of the temperature coefficients; they show, nevertheless, distinct minima.

*Cupric Chloride.*—This salt was heated for several hours in an atmosphere of dry hydrogen chloride at 160°–165°, then heated at the same temperature in a current of dry

<sup>1</sup> Loc. cit.



hydrogen and cooled in a current of the latter; lastly, it was heated in an air bath at about  $160^{\circ}$  for several hours and preserved as above described.

Lang<sup>1</sup> isolated the compound  $\text{CuCl}_2 \cdot 2\text{Pyr}$ .

TABLE XXI

V	$l_6$	$l_{25}$	$l_{50}$
25.0	0.053	0.062	0.074
50.0	0.066	0.076	0.086
100.0	0.088	0.098	0.111
200.0	0.130	0.146	0.171
500.0	0.203	0.216	0.216
1000.0	0.302	0.365	0.410

TABLE XXII

V	A	B	C
25.0	0.0073	0.0076	0.0082
50.0	0.0059	0.0052	0.0059
100.0	0.0045	0.0055	0.0053
200.0	0.0050	0.0068	0.0063
500.0	0.0027	0.0000	0.0014
1000.0	0.0084	0.0049	0.0072

The curves (Fig. XI) for cupric chloride show an apparent transition for the values of  $l_v$ . The equivalent conductivity increases steadily with increasing dilution. The large factor 100, by which  $l$  is multiplied, is responsible for the marked break in the curves. The temperature coefficients show minimum values.

Ley<sup>1</sup> obtained a blue solution when he dissolved cupric chloride in pyridine; this solution gave  $l_{30} = 0.05$ , in close agreement with the results given in this work for the same dilution. Ley assumes that the blue color of the pyridine solution is due to an undecomposed cupric chloride-pyridine compound and not to copper ions. Kohlschuetter<sup>2</sup> states

<sup>1</sup> Loc. cit.

<sup>2</sup> Ber. deutsch. chem. Ges., 37, 1153 (1904).

that cupric chloride dissolved in pyridine gives a blue solution, that is, the color of the solution corresponds to the color of the hydrated salt, and, since its molecular weight as found by the boiling-point method is normal, its color may be attributed to that of the undissociated cupric chloride. In these pyridine solutions there may be complexes of solvent and solute of the order of  $\text{CuCl}_2 \cdot 2\text{Pyr}$ , corresponding to  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ , or of a higher order. Naumann<sup>1</sup> states that cupric chloride dissolves in pyridine with evolution of heat,

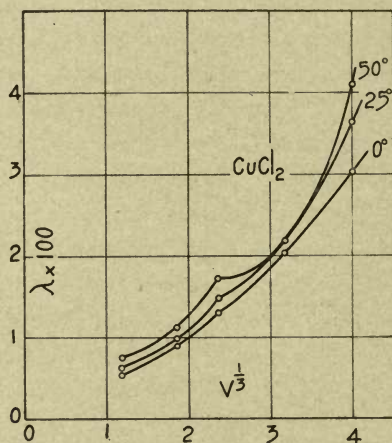


Fig. XI

giving a blue solution and therefore assumes that the complex  $\text{CuCl}_2 \cdot 2\text{Pyr}$  is present in the solution. All these investigators affirm that cupric chloride dissolved in pyridine gives rise to a blue solution. All of the cupric chloride solutions used in this work had a beautiful, deep green color without the least indication of a bluish tint and, furthermore, the solutions remained green for several months,—until finally rejected. On the other hand, in making one of the trial solubility tests, an attempt was made to weigh directly a sample of the dry cupric chloride. The salt absorbed

<sup>1</sup> Ber. deutsch. chem. Ges., 37, IV, 4609 (1904).



moisture so rapidly that accurate weighing was impossible. Although it was noticed that the edges of the salt mass had taken on a greenish blue color, the salt was quickly transferred and dissolved in pyridine, and, as might be expected, the solution was distinctly blue. When, however, the cupric chloride was quickly weighed by difference, a deep green solution was obtained. It is evident, therefore, that the blue color observed by Kohlschuetter, Lang, Ley and Naumann is due to the presence of a slight trace of moisture. It is safe to assert that the green color of a solution of cupric chloride in pyridine is due to the presence of  $\text{CuCl}_2 \cdot 2\text{Pyr}$ , and the blue color often obtained when supposedly dry cupric chloride is dissolved in the same solvent is due to the presence of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ . The values given by Lincoln<sup>1</sup> at  $25^\circ$  for  $l_v$  (recalculated from those given for  $\mu$ ) are much higher than the above or those given by Ley.<sup>1</sup>

*Copper Nitrate.*—The anhydrous salt was prepared by the method of displacement used by Kahlenberg.<sup>2</sup> A 0.1 N solution of silver nitrate in pyridine was treated with an excess of finely divided, reduced metallic copper and allowed to stand until the solution gave no test for silver.

Copper nitrate crystallizes from pyridine solutions as the complex  $\text{Cu}(\text{NO}_3)_2 \cdot 4\text{Pyr}$ .<sup>3</sup>

TABLE XXIII

V	$l_0$	$l_{25}$	$l_{50}$
10.0	9.68	12.94	14.96
20.0	5.00	7.21	8.88
40.0	8.57	11.60	14.16
100.0	12.08	16.43	20.43
1000.0	16.41	22.88	29.71
10,000.0	19.42	27.24	35.71

<sup>1</sup> Loc. cit.

<sup>2</sup> Jour. Phys. Chem., 3, 379 (1899).

<sup>3</sup> Grossmann: Ber. deutsch. chem. Ges., 37, 1253-7 (1904).

TABLE XXIV

V	A	B	C
10.0	0.0135	0.0062	0.0109
20.0	0.0176	0.0093	0.0155
40.0	0.0142	0.0088	0.0131
100.0	0.0144	0.0097	0.0138
1000.0	0.0158	0.0119	0.0162
10,000.0	0.0161	0.0124	0.0168

A study of Fig. XII discloses the fact that copper nitrate is peculiar in its behavior, in that, like the mercuric halides, it gives minimum conductivity values. After passing through the minima the values for  $l_v$  first increase at a moderate rate and then exceedingly slowly with increasing dilution.

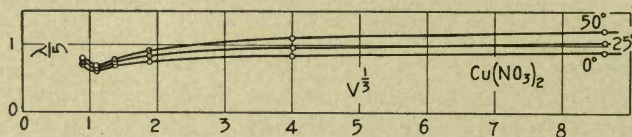


Fig. XII

Here again, the temperature coefficients show minimum values.

*Cadmium Nitrate.*—The pure anhydrous salt was prepared by the displacement of silver in a 0.1 *N* solution of silver nitrate by means of chemically pure cadmium.

TABLE XXV

V	$l_0$	$l_{25}$	$l_{50}$
10.0	0.141	0.160	0.122
20.0	0.322	0.348	0.288
40.0	0.402	0.433	0.340
100.0	0.694	0.733	0.630
1000.0	2.37	2.31	2.44
10,000.0	7.40	8.60	9.80



TABLE XXVI

V	A	B	C
10.0	0.0052	—0.0095	—0.0028
20.0	0.0033	—0.0070	—0.0021
40.0	0.0031	—0.0086	—0.0031
100.0	0.0023	—0.0056	—0.0018
1000.0	—0.0010	0.0023	0.0006
10,000.0	0.0065	0.0056	0.0065

The equivalent conductivities of cadmium nitrate (Fig. XIII) increase quite steadily with increase in dilution. The curves obtained by plotting the temperature coefficients are somewhat irregular, but in general show minima of negative value. The curves run quite closely together, diverging only to an appreciable extent in the more dilute solutions.

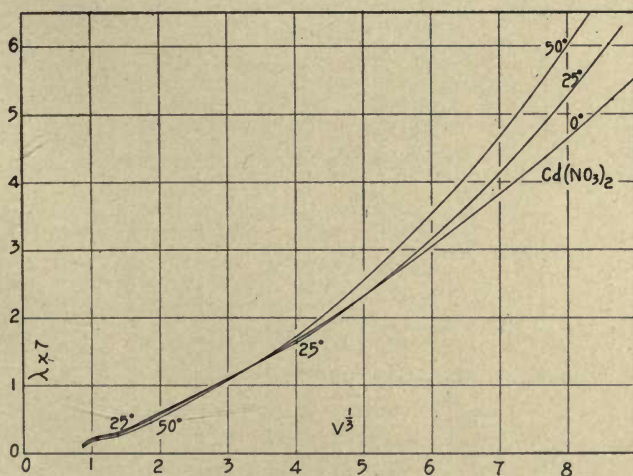


Fig. XIII

**Cobalt Chloride.**—The sample used was partially dehydrated *in vacuo* over phosphorus pentoxide, then heated in an atmosphere of dry hydrogen chloride at 140° for twenty-four hours, and finally in a current of dry hydrogen for fifteen hours. The product was of a pale blue color. Reitzenstein<sup>1</sup> prepared the compound  $\text{CoCl}_2 \cdot 4\text{Pyr}$ . Cobalt chloride

<sup>1</sup> Loc. cit.

dissolved in pyridine gives a red solution at 0°, a violet at 25°, and a deep purple solution at 50°.

TABLE XXVII

V	$l_0$	$l_{25}$	$l_{50}$
10.0	0.009 <sup>1</sup>	0.012	0.012
20.0	0.015	0.015	0.022
40.0	0.021	0.020	0.024
100.0	0.042	0.045	0.041
1000.0	0.220	0.230	0.310
10,000.0	0.600	1.000	1.100

TABLE XXVIII

V	A	B	C
10.0	0.0149 <sup>1</sup>	0.0319	0.0293 <sup>1</sup>
20.0	0.0019	0.0174	0.0101
40.0	—0.0021	0.0082	0.0028
100.0	0.0028	—0.0036	—0.0005
1000.0	0.0018	0.0139	0.0082
10,000.0	0.0267	0.0040	0.0167

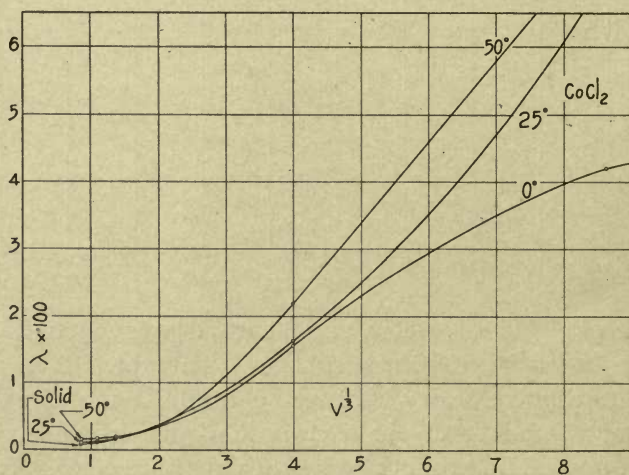


Fig. XIV

<sup>1</sup> Solid present.



Cobalt chloride in pyridine solutions is at best an exceedingly poor conductor. By some, its solutions are considered as non-conductors. Consequently, slight errors in the work are highly magnified. The results obtained show a continuous increase in equivalent conductivity with dilution for all temperatures. Again, Lincoln's<sup>1</sup> values for  $l_v$  at corresponding dilutions are very much higher than the values here quoted. The temperature coefficients are likewise subject to considerable error, yet even these show definite minima at which negative coefficients are observed.

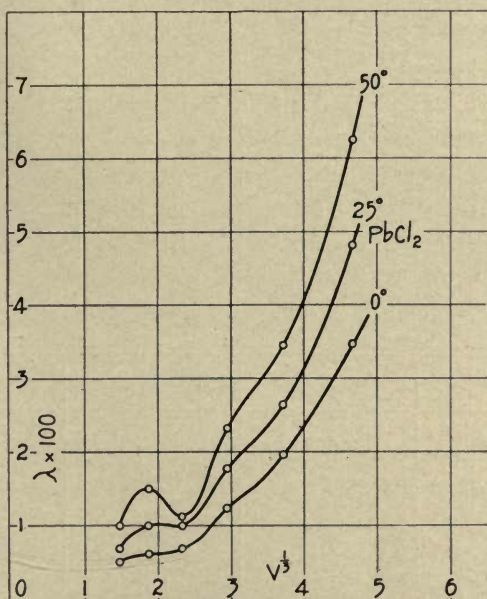


Fig. XV

Werner<sup>1</sup> and his co-workers found by the ebullioscopic method that cobalt chloride has the normal molecular weight in pyridine.

**Lead Chloride.**—The salt was precipitated from chemically pure lead nitrate by pure hydrochloric acid. It was then thoroughly washed with water and heated to dryness at 120°.

<sup>1</sup> Loc. cit.

Pyridine forms three crystalline compounds with lead chloride, e. g.,  $3\text{PbCl}_2 \cdot 4\text{Pyr}$ ,<sup>1</sup>  $4\text{PbCl}_2 \cdot 3\text{Pyr}$ ,<sup>2</sup> and  $\text{PbCl}_2 \cdot 2\text{Pyr}$ .<sup>3</sup> It crystallizes from aqueous solutions in the form of the anhydrous salt and should have small hydrating power and low temperature coefficients of conductivity. Jones and Winston<sup>4</sup> find, however, that the temperature coefficients in aqueous solutions are relatively high. Apparently the temperature coefficients are not entirely dependent upon the amount of solvent separating with the solute when solvates crystallize from solution.

TABLE XXIX

V	$l_0$	$l_{25}$	$l_{50}$
50.0	0.05	0.07	0.10
100.0	0.06	0.10	0.15?
200.0	0.07	0.10	0.11
400.0	0.12	0.18	0.23
800.0	0.20	0.26	0.35
1600.0	0.35	0.48	0.63

TABLE XXX

V	A	B	C
50.0	0.030	0.019	0.020
100.0	0.025	0.021	0.030?
200.0	0.019	0.005?	0.013
400.0	0.018	0.013	0.018
800.0	0.014	0.012	0.015
1600.0	0.016	0.012	0.016

### Discussion

The power of a solution to conduct electricity depends upon the dielectric constant of the solvent, the degree of dissociation of the electrolyte, the number of ions present and their velocities. The degree of dissociation is determined

<sup>1</sup> Zeit. anorg. Chem., **4**, 100-110 (1893).

<sup>2</sup> Ibid., **14**, 379-403 (1897).

<sup>3</sup> Jour. Phys. Chem., **15**, 373 (1912).

<sup>4</sup> Am. Chem. Jour., **46**, 368 (1912).



by the dielectric constant of the solvent and the electro-affinity of the ions. For a given potential gradient the ionic velocities are in turn dependent upon the viscosity of the solution, the mass or the volume of the ions. The mass and volume of either or both ions may be further augmented by combination with the molecules of the solute to form complex ions, or with the molecules of the solvent to form more or less highly solvated ions.

For solutions in a large number of solvents the molecular conductivity behaves normally, *i. e.*, it increases with increasing dilution. There are, however, numerous instances like those shown by the mercuric halides in pyridine in which the equivalent conductivity decreases, passes through a minimum and then rises with increase in the concentration of the solute. Such phenomena are considered by many as being incapable of explanation on the basis of the Arrhenius theory. That increase in molecular conductivity with increase in concentration in some organic solvents is peculiar only to the concentrated solutions has been shown by Pearce<sup>1</sup> and others. He, like Sachanov,<sup>2</sup> found that the molecular conductivity of various salts in aniline decreased with increase in dilution to a minimum and then increased normally upon further dilution.

Franklin<sup>3</sup> explains the increase in molecular conductivity with increasing concentration as due to an increase in auto-ionization, which more than compensates for the decrease in molecular conductivity due to an increase in viscosity.

In their study of the conductivity of various inorganic salts and non-salt organic solutes in the liquid halogen acids Archibald, McIntosh and Steele<sup>4</sup> found that the molecular conductivity increases with increasing concentration. They assumed that, while the original solute may of itself be incapable of ionizing in the solvent, it may combine with the

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<sup>1</sup> Unpublished results.

<sup>2</sup> Jour. Russ. phys. chem. Soc., **42**, 683-690 (1910).

<sup>3</sup> Loc. cit.

<sup>4</sup> Zeit. phys. Chem., **55**, 129 (1907).

solvent to form a complex solvent-solute molecule which behaves as an electrolyte. Accordingly, the number of complexes must increase with the concentration and, likewise, the molecular conductivity must increase, due to an increase in the total number of ions. These investigators used the expression

$$M_v = \alpha K' = \chi V^n,$$

where  $\alpha$ ,  $\chi$  and  $V$  represent the degree of dissociation, the specific conductance and the volume, respectively.  $K'$  is a constant and  $n$  is the number of simple molecules of solute combined with  $m$  molecules of solvent. By means of this relation they calculated the molecular conductivity and found it to increase normally with dilution. It is obvious that when  $\alpha$  is equal to unity,

$$M_\infty = K'.$$

Evidently these investigators did not consider the fact that the amount of solvation per molecule of solute will vary with the dilution and must necessarily decrease as the concentration of the solute is increased. Where solvation is possible it is difficult to conceive how the complex, say,  $(n)$  solute- $(m)$  solvent can remain unchanged throughout a wide range in concentration.

Sachanov has studied the molecular conductivity of various solutions in acetic and propionic acids<sup>1</sup> and in aniline, methylaniline and dimethylaniline.<sup>2</sup> In practically every case the molecular conductivity was found to increase with increasing concentration. All of these solvents have low dielectric constants and slight dissociating power. In a later article,<sup>3</sup> he states that a decrease in molecular conductivity with increasing dilution is just as characteristic for solvents with low dielectric constants as is an increase in molecular conductivity for solutions in solvents with high dielectric constants. He<sup>4</sup> asserts that electrolytic dissociation does

<sup>1</sup> Jour. Russ. phys. chem. Soc., 43, 526 (1911).

<sup>2</sup> Ibid., 44, 324 (1912); 42, 683 (1910).

<sup>3</sup> Zeit. phys. Chem., 80, 13 (1912).

<sup>4</sup> Ibid., 80, 20 (1912).



not depend solely on the magnitude of the dielectric constant, but also on the solvates and complex ions. The formation of such ions favors electrolytic dissociation because the electro-affinity of these complex ions is greater than that of the simple ions. In solvents with low dielectric constants only the complexes which yield complex ions of high electro-affinity can undergo electrolytic dissociation. The decrease in electrolytic conductivity in such solvents is explained as being due to the composition of these polymerized solute molecules on dilution.

An examination of the curves plotted from the data will show that the electrolytes used in this work are of two types. First, those which give minimum conductivity values at all temperatures, *viz.*, the mercuric halides and copper nitrate. Second, those like the nitrates of silver and cadmium, the chlorides of lithium, cobalt, copper and lead, the iodides of lithium and sodium, lithium bromide, and the thiocyanates of potassium and ammonium, which upon dilution give increasing values of  $l_v$ .

The phenomenon of the molecular conductivity increasing with increasing concentration is considered by some as being at variance with the Arrhenius theory. However, an attempt will be made in the present discussion to show that this anomalous behavior is due entirely to the presence and the properties of the polymerized solute molecules which are present in solutions showing such phenomena.

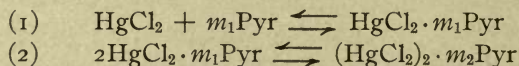
The most dilute solutions studied by Walden and Centnerszwer<sup>1</sup> correspond to those concentrations which give the minimum conductivity values in this work, and hence we have no experimental evidence as to the state of aggregation in the very dilute solutions. Assuming only the ionization of simple molecules, their results would seem to show that these molecules are ionized in the concentrated, but undissociated in the dilute solutions, which is contrary to common experience. That some ions are present at all dilutions is evident from the conducting power of these solutions.

<sup>1</sup> Zeit. phys. Chem., 55, 231 (1906).

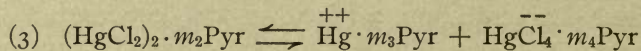
The abnormal boiling-point results noted must, therefore, be due to such an equilibrium between the various forms of the electrolyte present in the solution, *viz.*, simple and complex molecules, simple and complex ions and the pyridinated forms of each, as would give the molecular weights obtained.

Let us consider, as an example of the first type, the solutions of mercuric chloride, and what is said concerning them will apply, for the most part, to the other salts which give minimum conductivity. This salt is very soluble and has a strong tendency to combine with pyridine to form stable salts with pyridine of crystallization. Naturally, then, we would expect it to combine with still more pyridine when in solution in this solvent. Walden and Centnerszwer<sup>1</sup> have found that the mercuric halides exhibit a strong tendency to polymerize in pyridine solutions, just as they do in most solvents.

We should expect to find in these solutions the simple and polymerized molecules of mercuric chloride, the simple and complex ions and the solvated ions and molecules. The number and kind of each will depend upon the dilution. The equilibria between the different forms of the solute may be represented thus:



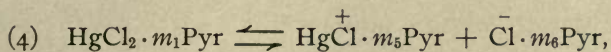
As the concentration of the solute is increased the equilibrium will naturally be disturbed and the resulting effect will be a corresponding increase in the concentration of the polymer. Hence the reaction will proceed from left to right, as in (2). It is evident from the increase in conductivity in the most concentrated solutions that the dissociation of the polymerized molecules must be greater than that of the simple molecules. The conditions of equilibria may be represented by the following relations:



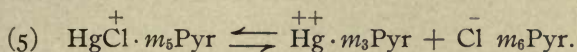
In the most dilute solutions where the simple molecules predominate, we shall have the equilibrium represented by

<sup>1</sup> Loc. cit.





and possibly to a slight extent,

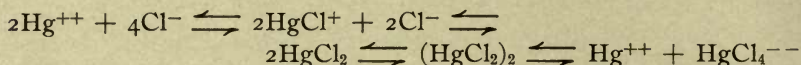


In the intermediate concentrations all of these equilibria will be found to a greater or lesser extent. The degree of pyridination of the various solute particles ( $m_1$ ,  $m_2$ , etc.) will depend upon the dilution.

Inasmuch as the molecular weight of mercuric chloride in pyridine approximates the normal value, and, therefore, the effect due to polymerization must approximately annul that due to dissociation and solvation, the extent of the polymerization must be slight, because the conductivity is low. Hence we may attribute to the polymerized molecules a strong ionizing power and, consequently, a high degree of dissociation in these solutions.

All the solutions used in the present work were made up under the assumption that no polymerization of the solute takes place. It is, therefore, evident that the actual normalities of the concentrated solutions with respect to the ionizing polymers are less than assumed in preparing the solutions. For example, if exactly one gram-molecular weight of mercuric chloride is dissolved in pyridine and then diluted to one liter and, if it is assumed that all the simple molecules combine in pairs to form single molecules of the polymerized form, the normality with respect to the polymer will be 0.5  $N$  instead of 1.0  $N$ , as would be the case, if no polymerization takes place. If, on the other hand, only a fraction of the simple molecules combine to form the polymerized form, the normality of the ionizing polymers will be still less, and will always be one-half the fractional molar concentration of the simple molecules which have become polymerized. If we are then dealing with ionizing polymers, the degree of dissociation for a given solution in the concentrated regions will be relatively much higher than it would be if we were actually dealing with the normality at which the solutions are originally made up.

In order to explain minimum conductivity the following equilibrium equation will be used as a guide:



In the concentrated solutions the ions present will result from the dissociation of the polymers. There will be only a very slight tendency towards simple ionization and this will be impeded by the repression of ionization due to the mercury ions. As the most concentrated solutions are dilute the equilibrium will be disturbed and polymers will change over into simple molecules in obedience to the law of mass action. Hence the concentration of the ions formed from the polymers will decrease, although the dissociation of the remaining polymers will become more and more complete with continued dilution. The result will be a decrease in the equivalent conductivity. As dilution is continued the influence of the simple ionization will soon become effective on account of the polymers being converted almost completely into simple molecules. These in turn furnish a preponderance of simple ions which will cause the repression of the complex ionization. The equivalent conductivity should, therefore, begin to rise again and continue to do so with an increase in dilution. This, then, would mean that the minimum values would be encountered for the equivalent conductivity. Of course viscosity changes as well as solvation effects are taking place with dilution. The latter would naturally change the sizes of the ions and, therefore, alter the freedom with which they would move. The decrease in viscosity would also result in greater freedom to the mobility of the ions. However, all these last mentioned factors would be subordinated to the changes in the concentrations of the various kinds of ions, as just outlined.

Solutions of silver nitrate, lithium bromide, lithium iodide, and the thiocyanates of ammonium and potassium all possess high conductivity values. The most concentrated solution of each is noticeably viscous. On the other hand,



cadmium nitrate and the chlorides of lithium, cobalt, copper and lead are only slightly soluble in pyridine. Their most concentrated solutions have apparently low viscosities. The equivalent conductivities shown by these electrolytes are very low. Hence, within the limits of these facts, the viscosity is not the predominating effect in their conductivity.

Another point in connection with the salts just mentioned is the fact that, generally speaking, the binary salts are the better and the ternary salts the poorer conductors.

The existence of minima of temperature coefficients of equivalent conductivity seems to be a general phenomenon in pyridine solutions. The solvation per molecular weight of the solute is greatest in the more dilute solutions. Owing to the greater concentrations of the solute, however, the concentrated solutions will contain a much greater percent of combined pyridine, the degree of solvation decreasing with increasing concentration. The instability of these solvates increases not only with increase in complexity but also with increase in temperature.

The minima of the temperature coefficients may be explained on the basis of viscosity and ionic solvation. We would expect the greatest temperature changes in the most concentrated solutions. Here the viscosity is greatest and the percent of pyridine locked up as that of solvation is at a maximum. The effect of the decrease in the complexity of the solvates due to a rise in temperature would be to increase the amount of the pure solvent. This in itself means a decrease in the viscosity of the solution. Then, too, the rise in temperature results in a decrease in the viscosity of the pure solvent. For these reasons the solvated ions, which in themselves may or may not have suffered an appreciable change, due to the rise in temperature, are able to migrate more rapidly. In the less concentrated solutions the viscosity changes due to a rise in temperature will be less pronounced. Hence the values of the temperature coefficients will decrease. While the decrease in the viscosity change

with dilution is going on the ionic solvation is increasing. The instability of the solvated ions with rise in temperature is also increasing with dilution. As the temperature is raised the decrease in the complexity of the solvated ions will cause an increase in their mobility. Thus we can readily understand how the solvated-ion effect can annul that of the viscosity. It is this condition which gives rise to the minimum temperature coefficient values. As the increase in dilution continues the ion solvation effect becomes the sole factor and hence we obtain a steady increase in the values of the temperature coefficients.

Another point to be noted is that the temperature coefficients are greater between  $0^{\circ}$  and  $25^{\circ}$  than those obtained for the interval  $25^{\circ}$ – $50^{\circ}$ . Since the decrease in the complexity of the solvated ions caused by a rise in temperature must be greatest in the region of greatest complexity, a greater change should be expected at temperatures favorable to a higher degree of complexity, *i. e.*, between  $0^{\circ}$  and  $25^{\circ}$ .

No explanation can be offered for the negative temperature coefficients in the cases of lithium bromide, sodium iodide, cobalt chloride and cadmium nitrate.

Comparing the magnitudes as well as the relative changes of temperature coefficients with dilution for the different electrolytes there seems to be no direct relation between these and the amount of pyridine with which they are combined when they crystallize from solution.

In general, the binary salts show the highest equivalent conductivity. The ternary give the lowest. There are, however, two notable exceptions to this generalization: lithium chloride, a binary salt, gives very low, while copper nitrate, a ternary salt, gives comparatively high values of the equivalent conductivity.

So far as the effect of solvation on conductivity is concerned, there is no reason for assuming the combination of solute and solvent as essential to the increase of electroaffinity, as Sachanov<sup>1</sup> has done. After the ions are once

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<sup>1</sup> Loc. cit.



formed then combination of the same with the solvent may modify their electro-affinity to some extent.

Inasmuch as the dielectric constant of pyridine (20) varies little within the temperature range studied its effect must be practically constant throughout. Since pyridine is considered as a non-associated solvent<sup>1</sup> this factor would not enter into the problem.

### Summary

A study of the equivalent electrical conductivity of solutions of fifteen salts in pyridine has been made at three temperatures, *viz.*, 0°, 25° and 50°.

Two classes of electrolytes are to be observed. (1) Those for which the equivalent conductivity increases throughout with increasing dilution; (2) those which give minimum values of equivalent conductivity.

The values of the temperature coefficients between 0° and 25° are higher than those between 25° and 50°. An explanation is offered.

An explanation for the minimum values of equivalent conductivity has been advanced.

It has been shown that the anomalous behavior in equivalent conductivity is due entirely to the presence and properties of the ionizable polymerized solute, which predominates in the concentrated solutions.

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<sup>1</sup> J. L. R. Morgan: Jour. Am. Chem. Soc., 30, 1068 (1908).

### BIOGRAPHY.

The author was born in Minneapolis, Minnesota, February 9, 1885, and began his school career in the public schools of the same city, graduating from the eighth grade in 1899. He next attended the East Minneapolis High School, receiving a diploma in 1903. A course in Analytical Chemistry was then pursued at the University of Minnesota, and the degree B.S. in Chemistry was received in 1908. The following year the degree M.S. was conferred upon him at the same institution. While at the University of Minnesota he assisted in Qualitative Analysis for five years. From 1909 to 1913 he held a position as Instructor in Chemistry at the State University of Iowa, and since then has been instructing in Chemistry at the State University of North Dakota.



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E. X. A.













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